171. *A Criterion for the Mechanism of the Reaction between Alkyl Halides and Hydroxylic Solvents. Reactions of* tert.*-Butyl Chloride.*

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A means of distinction between the two mechanisms of nucleophilic aliphatic substitution, suitable for application to those first-order reactions in which the reagent is in large excess, is based on the circumstance that in bimolecular substitution the product is determined in a reaction whose rate can be measured, whilst in unimolecular substitution it is formed, not in the rate-measured process, but in a subsequent fast reaction :

$$\mathrm{Y} + \mathrm{R}\vdots\!-\!\mathrm{X} \longrightarrow \mathrm{Y}-\mathrm{R} + \mathrm{X} \quad . \quad . \quad . \quad \text{(Bimolecular)}$$

$$\left.\begin{array}{l} \mathrm{R}\vdots\!-\!\mathrm{X} \longrightarrow \mathrm{R}^+ + \mathrm{X}\ \text{(slow)} \\ \mathrm{Y} + \mathrm{R}^+ \longrightarrow \mathrm{Y}\text{—}\mathrm{R}\ \text{(fast)} \end{array}\right\} \quad . \quad . \quad \text{(Unimolecular)}$$

Olson and Halford having advanced a successful quasi-thermodynamic expression for the interpolation of reaction rates in binary solvent mixtures from observed rates in two mixtures of different composition, we can apply the principle stated as follows. Consider the simultaneous hydrolysis and alcoholysis of an alkyl halide in aqueous alcohol. Whatever may be the mechanism, the two constants that can be derived from rate measurements at two solvent compositions will permit calculation of the rate at some other solvent composition. If the mechanism is bimolecular, the same two rate-derived constants will also allow calculation of the composition of the substitution product (alcohol plus ether), because this is formed in the reaction whose rate we measure; whereas if the mechanism is unimolecular, the measured rates will have no connexion with the composition of the product, which is formed in a different reaction-stage. Thus by determining both rates and product compositions we can discover the mechanism. This criterion has been applied to the hydrolysis and methyl- and ethyl-alcoholysis of *tert.*-butyl chloride. Despite the excellence of the rate interpolations, the product compositions are widely different from those calculated by Olson and Halford's formula on the assumption that the mechanism is bimolecular. It is concluded that the mechanism is unimolecular, in agreement with other evidence.

The four methods now available for the solving of such problems are summarised, and their limitations are noted.

The theory of aliphatic substitution sketched by Ingold and Rothstein (J., 1928, 1217; cf. Ingold and Patel, *J. Indian Chem. Soc.*, 1930, **7**, 95) and generalised by Hughes, Ingold, and Patel (J., 1933, 526) and Hughes and Ingold (J., 1935, 244) recognises two main classes of substitution, determined by the electrical affinities of the reagent, two divisions within each class, depending on whether one or two bonds are exchanged, and, for every one of these kinds of substitution in solution, two typical mechanisms, one involving replacement in a single stage and the other preliminary ionic fission. This paper is a contribution to the problem of distinguishing between these mechanisms.

The method to be considered is in principle general, but we shall confine explicit discussion to substitutions by nucleophilic reagents which effect an exchange of one bond. The first mechanism, termed " bimolecular," may then be formulated

$$\mathrm{Y} + \mathrm{R}\vdots\!-\!\mathrm{X} \longrightarrow \mathrm{Y}\text{—}\mathrm{R} + \mathrm{X} \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{S_N2})$$

where the charges on Y and X are unspecified, being subject only to the restrictions imposed by the electron transfer from Y to R and from R to X. The reaction is normally of the second order, and may be of the first order, *e.g.*, if the reagent Y is in very large excess. The second mechanism, which we term "unimolecular," may be expressed

$$\left.\begin{array}{r}\mathrm{R}\!\vdots\!\!-\!\mathrm{X}\longrightarrow\mathrm{R}^{+}+\mathrm{X}\ (\text{slow})\\ \mathrm{Y}+\mathrm{R}^{+}\longrightarrow\mathrm{Y{-}R}\ (\text{rapid})\end{array}\right\}\quad\cdots\cdots\quad(\mathrm{S_N1})$$

where the electron transfers are as before. Here the separation of bond-fission and bond-formation into stages, of which the former controls the rate, causes the reaction to exhibit first-order kinetics, independently of the relative concentrations of the reagents. We have emphasised (cf. Hughes and Ingold, *loc. cit.*) that the solvent must play an especially important part in the ionic fission, since in all spontaneous ionisations it is solvation which reduces the activation energy to accessible values; and, furthermore, that the transition from one mechanism to the other cannot be absolutely sharp, as there must be degrees of time-separation between the bond-breaking and bond-forming processes (cf. Hughes, Ingold, and Patel, *loc. cit.*; Gleave, Hughes, and Ingold, J., 1935, 236; Hughes, Ingold, and Shapiro, J., 1936, 225).

When the entering substituent comes from a reagent present in small and controllable concentration there is usually no difficulty in distinguishing these mechanisms kinetically. Thus, kinetic data show that the action of halide ions on α-phenylethyl halides is bimolecular in acetone and unimolecular in sulphur dioxide, whilst the attack of halide ions on alkylsulphonium ions is unimolecular even in acetone. Since these examples of kinetically established unimolecular reactions were recalled (Hughes and Ingold, *loc. cit.*), others have arisen in the action of water and chloroacetate ions on *tert.*-butyl chloride in formic acid as solvent, and of halide ions, water, and amines on benzhydryl halides in sulphur dioxide (Bateman and Hughes, J., 1937, 1187, and unpublished work).*

There is, however, an important class of examples, *e.g.*, the hydrolysis of alkyl halides in aqueous solvents, in which the entrant group may come from a relatively large quantity of the solvent. For these reactions, kinetics are not determinative; and other criteria of mechanism have been advanced. For example, we have concluded that the water-hydrolysis of α-bromopropionic acid (molecules) is bimolecular, whilst that of *tert.*-butyl chloride is unimolecular, but not on kinetic grounds, as both reactions are of the first order. We shall summarise the available methods of making such decisions after having illustrated a new method, which, we think, has considerable potential importance.

This method arises as an extension of an attempt by Olson and Halford (*J. Amer. Chem. Soc.*, 1937, **59**, 2644) to solve the same problem. The example is the simultaneous hydrolysis and alcoholysis of *tert.*-butyl chloride in aqueous-alcoholic solvents. This total first-order reaction was originally examined by Hughes (J., 1935, 255), who found that the rate was unaffected by hydroxonium or by hydroxide ions, and increased with the ionising power of the solvent, *e.g.*, with an increase in the water content of aqueous alcohol. Hughes concluded that the reaction was unimolecular.

With reference to the effect of such variations of solvent composition, Olson and Halford considered the consequence of supposing the reaction to be bimolecular. First, they set up the rate equation

$$\text{Rate} = (k_a p_a + k_w p_w) p_{\mathrm{RCl}}$$

where k_a and k_w are specific rate constants for pure alcohol and pure water, and p_a and p_w are the partial vapour pressures of these constituents of the solvent mixtures, p_{RCl} being the partial vapour pressure of the *tert.*-butyl chloride. From observed rates at two extremes of solvent composition, the constants, k_a and k_w, were obtained; and these were then used in order to interpolate for rates at intermediate solvent compositions. Furthermore, from the assumptions made it followed that the two terms $k_o p_a p_{\mathrm{RCl}}$ and $k_w p_w p_{\mathrm{RCl}}$ respectively represent the rates of formation of *tert.*-butyl alkyl ether and *tert.*-butyl alcohol; so that the authors were able also to calculate the composition of the reaction product corresponding to each solvent mixture. Using Hughes's rate data for mixtures of ethyl

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* W. Taylor's conclusions in this field will be discussed in a forthcoming criticism.

alcohol and water, and new results of their own for mixtures of methyl alcohol and water, they showed that the rate-interpolation formula worked extremely well. They therefore concluded that the reaction was bimolecular.

It is, however, questionable whether any conclusions at all should be drawn at that stage of the investigation. Olson and Halford did not consider how the theoretical consequences of the unimolecular mechanism compare and contrast with those of its alternative, and they did not attempt to ascertain whether their calculated compositions of the reaction product agreed with experiment. This, as we shall show, is the crucial point.

The rate formula given depends on the idea that the transition state of reaction constitutes a mode of escape (in the thermodynamic sense) for all participating entities, whose tendency to form a transition state is thus likely to be closely correlated with other measures of fugacity, *e.g.*, vapour pressure. Although it is not altogether clear that Olson and Halford's treatment of the transition state is formally correct, we should certainly expect a rate-interpolation formula based on a mixture law for the fugacities of the solvent components to have much better success than any similar function of concentrations, at least where there is any marked lack of proportionality between fugacity and concentration. But this holds generally for reactions in solution, inasmuch as the solvent always enters into the transition state of such reactions. It holds *inter alia* for the slow stage of the unimolecular mechanism, and, since the measured reaction rate is the rate of this stage, the constants k_a and k_w that we can obtain from observed rates should enable to us calculate the dependence of the rate of the slow stage, *i.e.*, of the experimental rate, on the solvent composition. On the other hand, it is characteristic of the unimolecular mechanism that the products (in our case the butyl alcohol and butyl alkyl ether) are not determined in the reaction stage whose rate is measured : they are formed in subsequent fast reactions, which may also be subject to rate laws expressible in terms of fugacities, although the specific constants involved are experimentally inaccessible; it is from *these* constants, if we knew them, that we might be able to calculate the composition of the reaction product, not from the constants found kinetically. Therefore the essential thing to do in order to obtain a distinction between the two mechanisms is to ascertain whether the measured specific rate constants that are successful in the rate interpolation hold also for the calculation of the composition of the product. If they do, and do so consistently, then that indicates that the products are formed in the reaction stage whose rate is measured; and if they do not, then it shows that the products are formed otherwise than in the rate-measured stage. Only with such evidence should we feel justified in concluding in the former case that the reaction is bimolecular, and in the latter that it is unimolecular.

We are able to supply the required data for the hydrolysis and alcoholysis of *tert.*-butyl chloride. Using three mixtures of ethyl alcohol and water and three of methyl alcohol and water, for each of which Olson and Halford calculated the proportion of *tert.*-butyl alkyl ether that should be formed if the reaction is bimolecular, we have experimentally determined the proportion in which ether is formed. We have, of course, ascertained that, under the conditions used, there is no interconversion of products once they are formed. The actual products are *tert.*-butyl ethyl or methyl ether, *tert.*-butyl alcohol, and *iso*butylene. The last we have regarded as material side-tracked from the substitution processes, but the proportions are rather small and therefore it makes no great difference whether or not we include it amongst the products on the basis of which the percentage of ether is expressed. The results are in Table I, from which it will be seen that the observed proportions of ether are far larger (2—3 times) than the proportions calculated by Olson and Halford from rate data. The differences are very much greater than the errors inherent either in the experiments or in the calculations. We conclude that the substitution products are formed otherwise than in the reaction stage whose rate is observed. Therefore, by this as by previous tests, the reaction is essentially unimolecular.

For convenience we summarise the four chief methods now available for the diagnosis of reaction mechanism in those first-order substitutions in which the direct kinetic method is unavailable on account of the fact that the entrant group is derived from a large quantity of solvent. We note also the principal limitations associated with each method.

TABLE I.

Composition of Products of Reaction of tert.*-Butyl Chloride with Aqueous-alcoholic Solvents at 25°, and Comparison with Olson and Halford's Theoretical Values.*

	Composition of solvent. (mols. %).		Composition of product. (mols. %).			$\frac{100 \times \text{Ether}}{\text{Alcohol} + \text{Ether}}$.	
Solvent.	ROH.	H_2O.	Olefin.	Ether.	Alcohol.*	Calc.†	Found.
EtOH + H_2O	31·7	68·3	*ca.* 13 [a]	15·5	71·5	8	18
	55·3	44·7	17 [b]	27	56	11	33
	73·6	26·4	*ca.* 22 [c]	41	37	18	53
MeOH + H_2O	51·0	49·0	9	36	55	17	40
	71·6	28·4	13	59	28	29	68
	83·6	16·4	*ca.* 18 [d]	68	14	43	83

* By difference. † Calculations by Olson and Halford (*loc. cit.*).

[a] Approximately estimated by multiplying the following olefin figure (*b*) by the ratio of the proportions in which olefin is formed from *tert.*-amyl chloride in solvents having the compositions of the first two in the table (Hughes and MacNulty, J., 1937, 1283).

[b] Cooper, Hughes, and Ingold, J., 1937, 1280.

[c] Approximately estimated from the previous olefin figure (*b*) by means of considerations similar to those explained above (*a*).

[d] Approximately estimated from two previous olefin figures as explained.

(1) The first depends on the large effects arising from changes of structure in the compound substituted on the rate of reaction; for, in agreement with Evans and Polanyi (*Trans. Faraday Soc.*, 1936, **32**, 1333), we regard the logarithm of the rate as a more useful index than the Arrhenius critical energy as usually determined, though either can be used when the differences are sufficiently great. In substitution by nucleophilic reagents, electron accession to the seat of substitution decelerates the bimolecular reaction, provided the mechanism is well removed from bimolecular–unimolecular transition, and it strongly accelerates the unimolecular reaction universally. Whether or not a substitution is well removed from transition can usually be discovered by examination of an extended range of structures (papers of Hughes or Ingold cited; cf. Hughes, *Trans. Faraday Soc.*, 1938, **34**, 185; further examples in most other papers of this series).

(2) The second method utilises the effect on reaction rate of changes in the reagent, and especially on the action, or absence of action, of reagents which are much more strongly acidic or basic than the solvent. If vastly more powerful reagents than the solvent do not influence the rate, we conclude that such reagents are unable to affect the form of the main energy barrier; and therefore that they, and *a fortiori* the solvent itself, give up the entrant group after this main barrier has been passed. If, on the contrary, such strong reagents do affect the rate, then that means that in their presence a bimolecular reaction occurs; but it remains an open question, so far as this test is concerned, whether or not the same is true for the reaction with the solvent (Hughes and Ingold, *loc. cit.*).

(3) This is the method now illustrated, which employs the effect of solvent variation. Cases have been noted (*idem, ibid.*) in which we expect, and find, qualitatively opposite effects of solvent changes on the rates of bimolecular and unimolecular substitutions; but in all these cases an ionic reagent is involved, whose concentration can be controlled, so that they do not belong to the present problem. Just the same is true of effects (Cowdrey, Hughes, and Ingold, J., 1937, 1208) arising from the addition of neutral salts. Thus the method of solvent variation first becomes generally useful with the present development, to which the way was prepared by Olson and Halford.*

(4) Finally, there is the stereochemical method, limited, of course, to substitutions at an asymmetric centre. No outline need be given, as the matter has recently been fully discussed (Hughes, Ingold, and others, J., 1937, 1196, *et seq.*; Hughes, *Trans. Faraday Soc.*, 1938, **34**, 202).

These methods are just as available when the direct kinetic method can also be em-

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* The method is more useful than yet appears, because a second general criterion of mechanism, which will be explained and applied later, can be based on Olson and Halford's valuable work.

ployed; but their value is naturally greater when the reaction order fails to give the information.

EXPERIMENTAL.

Materials.—*tert.*-Butyl chloride of the quality used formerly (J., 1935, 255) had b. p. 50·6—50·8°/766 mm. Absolute ethyl and methyl alcohols were purified and fully dried by Lund and Bjerrum's method (*Ber.*, 1931, **64**, 210). Aqueous mixtures are specified by volume, *e.g.*, " 60%-EtOH " means the mixture made from 6 vols. of ethyl alcohol and 4 vols. of water. Ethyl *tert.*-butyl ether, prepared by heating *tert.*-butyl bromide with ethyl alcohol, with periodic neutralisation by means of ethyl-alcoholic sodium ethoxide, was well washed with water, dried, and distilled once from barium oxide and twice from potassium; it then had b. p. 71·5—72°/746 mm. Methyl *tert.*-butyl ether, prepared similarly, had b. p. 55—56°/769 mm.

Estimation of tert.*-Butyl Ethyl and Methyl Ethers in Reaction Mixtures from* tert.*-Butyl Chloride and Aqueous Ethyl and Methyl Alcohols.*—The physical properties of the constituents of the reaction mixtures render the quantitative isolation of these ethers difficult. Extraction with solvents proved unsatisfactory. The method adopted, which we claim to give reliable estimates of the ethers, was first to carry out an " isolation experiment " in which the reaction mixture was fractionated after dilution with water and the ether was isolated as described below for a typical case; and then to proceed with a parallel " recovery experiment " on a synthetic solution corresponding in all respects to the completed reaction mixture, except for the omission of olefin, which in any case escapes from unsealed vessels. Although there were minor variations of procedure in the different isolations, each recovery experiment was carried out *exactly* like the corresponding isolation experiment. It was found possible to recover 61—67% of the ether in a state of complete purity. Further experiments with synthetic solutions showed that this degree of uniformity in the recovery obtained over a considerably wider range of ether concentrations than actually arose in the isolation experiments, holding, to quote the extreme examples, for synthetic solutions containing the equivalent of as little as 1·6%, or as much as 100%, of ether. (The lowest and the highest estimate of ether in the isolation experiments were 15·5% and 68%.)

Isolation and recovery experiments were carried out with the following media: " 60%-," " 80%-," and " 90%-EtOH," and " 70%-," " 85%-," and " 92%-MeOH." For the isolation experiments in " 90%-EtOH " and " 92%-MeOH," 25 c.c. of *tert.*-butyl chloride were dissolved in the medium, a few drops of phenolphthalein added, and the whole was made up to 500 c.c. For " 85%-MeOH " the quantities were 40 c.c. of the chloride made up finally to 800 c.c.; whilst for the other media they were 50 c.c. of the chloride made up to 1000 c.c. The mixtures, kept in stoppered bottles in a thermostat at 25·0° ± 0·02°, were maintained nearly neutral by running in as necessary a solution of sodium hydroxide in the appropriate medium. This was intended as a precaution against any interconversion of products, which does under some conditions take place in acid media. We showed, however, by blank isolation and recovery experiments, in the former of which different proportions of *tert.*-butyl alcohol and *tert.*-butyl alkyl ether, in particular, pure *tert.*-butyl alcohol, replaced the *tert.*-butyl chloride, that the alcohol and ether undergo no trace of interconversion even under much more acidic conditions than obtained in the experiments summarised. We already knew from previous work (Cooper, Hughes, and Ingold, *loc. cit.*; Hughes and MacNulty, *loc. cit.*) that there could be no interconversion between *iso*butylene on the one hand and *tert.*-butyl alcohol and its alkyl ether on the other under the conditions employed.

In all the experiments with *tert.*-butyl chloride, its initial concentration was 0·45M.; its hydrolysis and alcoholysis would therefore change the concentrations of the solvent components by amounts of that order of magnitude. The neutralisation will produce a further change of comparable magnitude but in the opposite direction. As the most dilute solvent component in any of the mixtures (the water in the " 92%-MeOH ") was of concentration 16M., all solvent compositions may be regarded as sufficiently constant throughout reaction for the purposes of the comparison of Table I.

In illustration of the experimental method we now give details of the isolation of methyl *tert.*-butyl ether from the reaction product formed in " 85%-MeOH." The reaction mixture, after dilution with water (500 c.c.), was distilled with an 8-pear column to give the following fractions: (1*a*) 13 c.c., b. p. 51—65°; (1*b*) 20 c.c., b. p. 65—70°; (1*c*) 20 c.c., b. p. 70—71·6°; (1*d*) 80 c.c., b. p. 71·6—73°. With water (6 c.c.), 1*a* gave an upper layer, which was washed with water, whilst 1*b*, 1*c*, and 1*d* gave no separation of layers. Fractions 1*b* and 1*c*, water, and the washings from 1*a*, were combined and distilled: (2*a*) 13 c.c., b. p. up to 64°; (2*b*) 6 c.c.,

b. p. 64—82°. With water, 2*a* gave an upper layer, which was washed with water, whilst 2*b* gave no separation. Fraction 1*d* together with water was distilled : (3*a*) 2 c.c., b. p. up to 64°; (3*b*) 8 c.c., b. p. 64—75°. Water produced no separation of layers with either fraction. All washings and fractions which gave no separation with water were now combined, and, with added water, distilled : (4*a*) 6 c.c., b. p. up to 64°; (4*b*) 4 c.c., b. p. 64—80°. With water, 4*a* gave a top layer, which was washed with water, whilst 4*b* gave no separation. The washings from 4*a*, together with 4*b* and added water, were distilled : (5*a*) 2 c.c., b. p. up to 70°. Addition of water and calcium chloride gave an upper layer. The top layers (crude ether) from 1*a* (6 c.c.), 2*a* (9 c.c.), 4*a* (3 c.c.), and 5*a* (1 c.c.) totalled 19·0 c.c. A portion (9·8 c.c.) of this was subjected to the following distillations : (i) From fused barium oxide : yield 9·2 c.c., b. p. 52—56°. (ii) From potassium : yield 8·5 c.c., b. p. 54—56°. (iii) From potassium : yield 7·9 c.c., b. p. 55—56° (Found : C, 67·5; H, 13·6. Calc. for $C_4H_9\cdot O\cdot CH_3$: C, 68·2; H, 13·6%. *Note* : The analyses for methyl ethers were all slightly low for carbon, and this was not rectified by further distillation.) The over-all yield is thus 19·0 × 7·9/9·2 = 16·3 c.c.

The corresponding recovery experiment was carried out with the following solution : 960 c.c. of " 85%-MeOH " (the excess of this over the amount used to make up the *tert.*-butyl chloride to 800 c.c. in the isolation experiment being equal to the volume of the alkali solution added), 21 g. of sodium chloride, 8 g. of *tert.*-butyl alcohol, a few drops of phenolphthalein solution, a few drops of a solution of sodium hydroxide in " 85%-MeOH," and 25·0 c.c. of methyl *tert.*-butyl ether. By an identical isolation process, 19·7 c.c. of crude ether were recovered, which by the above three-stage rectification process gave 15·3 c.c. of the pure ether.

Numerical particulars of the whole series of experiments are summarised in Table II. All yields quoted are those of material fully rectified as above described, and analysed.

TABLE II.

Estimations of tert.*-Butyl Methyl and Ethyl Ethers.*

Medium.	H_2O content, mols. %.	Initial Bu$^{\gamma}$Cl. G.	Vol. (c.c.) of solution.		Pure ether isolated.		Analyses of ether,* %.		Percentage recovery (by expt.).	Ether formed † (mols. %).
			Initial.	Final.	G.	Mols. %.	C.	H.		
60%-EtOH	68·3	42·0	1000	1150	4·7	10·2	70·5	13·5	65·5	15·5
80%- ,,	44·7	42·0	1000	1200	7·5	16·2	70·6	13·7	60·6	26·7
90%- ,,	26·4	21·0	500	700	6·35	27·3	70·2	13·8	67·2	40·6
70%-MeOH	49·0	42·0	1000	1200	8·8	22·1	67·6	13·3	61·2	36·0
85%- ,,	28·4	33·6	800	1000	11·6	36·3	67·5	13·6	61·2	59·3
92%- ,,	16·4	21·0	500	700	8·6	43·0	67·5	13·6	62·9	68·4

* Calc. for Bu$^{\gamma}$OEt : C, 70·6; H, 13·7%. Calc. for Bu$^{\gamma}$OMe : C, 68·2; H, 13·6%.

† These estimates are believed to be correct to about ±4% of the figures listed.

Estimation of iso*Butylene formed from* tert.*-Butyl Chloride and Aqueous Alcohol.*—Estimations were carried out in " 70%-MeOH " and " 85%-MeOH." It was necessary to steer between two possible disturbances (Cooper, Hughes, and Ingold, *loc. cit.*; Hughes and MacNulty, *loc. cit.*). One is that, in a solution which is allowed to become too strongly acid, the olefin after being formed slowly disappears by adding on the solvent. The other is that in strongly alkaline solution there is a small incursion of bimolecular olefin formation, *i.e.*, elimination of hydrogen chloride by direct attack of hydroxide or methoxide ions; this increases the proportion of olefin formed above the value characteristic of weakly alkaline or acidic solutions. Between the limits thus imposed there is a wide " safe " region, and for convenience we have used the region between 0·1N-alkali and the neutral point, solutions originally of about the alkalinity stated being allowed to run nearly neutral.

The method was as follows. Sodium (about 0·23 g.) was dissolved in the medium; *tert.*-butyl chloride (about 1 c.c.) was then added, and the whole made up to 100 c.c. Portions of 5 c.c. were separately sealed up in bulbs, which were placed in the thermostat at 25·0°. Initial estimations of alkali and olefin were carried out as soon as the reaction mixture had been made up. Alkalinity values were found by breaking the bulbs in 100 c.c. of absolute ethyl alcohol and titrating with 0·0495N-acid, lacmoid being used as indicator. The loss of alkalinity during reaction measures the decrease in concentration of *tert.*-butyl chloride between the initial and the final measurements. Olefin was estimated by a standardised bromometric method as follows. The bulbs were cooled by shaking for 1 min. in a carbon dioxide–alcohol freezing mixture, dried externally, and then broken under a mixture of chloroform (70 c.c.), 0·0495N-acid (15 c.c.)

and ice-water (20 c.c.). The whole having been shaken, the chloroform layer was run off, washed with ice-water (50 c.c.), and dried for 5 mins. with calcium chloride. A solution (10 c.c.) of bromine in chloroform, saturated with hydrogen bromide, and standardised immediately before and after use, was then added and allowed to interact with the olefin for 5 mins. Then the unconsumed bromine was estimated as usual by titration with 0·0189N-thiosulphate after addition of potassium iodide and water. Corresponding to the initial and the final alkali determinations, three initial and three final estimations of olefin were carried out for each solvent. The initial olefin values measure the small amount of *iso*butylene produced during the making up of the solutions together with any trace of unsaturated material that may have been present in the reagents. There is no error due to the volatility of *iso*butylene : a full investigation of this method by Mr. S. Masterman has shown that it gives reliable results even with propylene. Thus the difference between the initial and final olefin values represents *iso*butylene formed during the measured disappearance of *tert.*-butyl chloride.

The results are exemplified below for " 85%-MeOH," and are summarised for the two media in Table III.

Estimations of alkali (in terms of the volume of 0·0495N-acid equivalent to 5 c.c. of reaction mixture) : Initial, 9·72 c.c. Final, 1·12 c.c. Loss, 8·60 c.c.

Estimations of olefin (in terms of the volume of 0·0189N-thiosulphate equivalent to 10 c.c. of the solution of bromine in chloroform, this being the quantity used in association with 5 c.c. of reaction mixture) :

(1) Initial : (*A*) Standardisation of bromine solution: Before the estimation, 9·59 c.c. After the estimation, 9·42 c.c. Mean, 9·50 c.c. (*B*) Measurement of residual bromine after reaction with olefin : 8·40, 8·28, 8·07 c.c. Mean, 8·24 c.c. (*C*) Bromine uptake : 9·50 − 8·24 = 1·26 c.c.

(2) Final : (*A*) Mean, 8·60 c.c. (*B*) Mean, 1·25 c.c. (*C*) 7·35 c.c. Therefore olefin formed = (2*C*) − (1*C*) = 7·35 − 1·26 = 6·09 c.c.

TABLE III.

Estimations of iso*Butylene.*

(Consumption of Bu$^\gamma$Cl in c.c. of 0·0495N-acid, and formation of C_4H_8 in c.c. of 0·0189N-thiosulphate, each equivalent to 5 c.c. of reaction solution.)

Medium.	Consumption of Bu$^\gamma$Cl.	Formation of C_4H_8.	Yield of C_4H_8 (mols. %).
70%-MeOH	8·25	4·0	9
85%- „	8·60	6·1	13

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